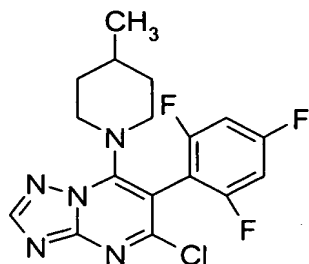


Fungicidal mixtures

Description

5 The present invention relates to fungicidal mixtures comprising, as active components,

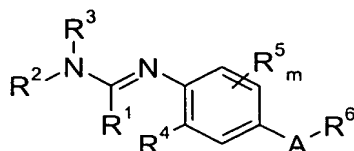
- 1) the triazolopyrimidine derivative of the formula I



and

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- 2) a phenylamidine derivative of the formula II



II

in which the variables are as defined below:

- 15 R^1 is hydrogen, C_1 - C_8 -alkyl, C_2 - C_8 -alkenyl or C_2 - C_8 -alkynyl which are unsubstituted or may be substituted by one to three groups R^a :

- 20 R^a is halogen, C_1 - C_8 -alkoxy, C_1 - C_8 -haloalkoxy, C_1 - C_8 -alkylthio or phenyl which may be substituted by halogen, C_1 - C_8 -alkyl, C_1 - C_8 -haloalkyl, C_1 - C_8 -alkoxy, C_1 - C_8 -haloalkoxy or C_1 - C_8 -alkylthio;

- 25 R^2, R^3 may be identical or different and are hydrogen, cyano, C_1 - C_8 -alkyl, C_2 - C_8 -alkenyl, C_2 - C_8 -alkynyl, C_1 - C_8 -alkoxy, C_1 - C_8 -alkoxyalkyl, benzyloxy or C_1 - C_8 -alkylcarbonyl which are unsubstituted or may be substituted by one to three groups R^a ;

- R^4 is hydrogen, C_1 - C_8 -alkyl, C_2 - C_8 -alkenyl or C_2 - C_8 -alkynyl which are unsubstituted or may be substituted by one to three groups R^b :

- 30 R^b is one of the groups mentioned under R^a , cyano, $C(=O)R^c$, $C(=S)R^c$ or $S(O)_pR^c$,

5 R^c is C_1 - C_8 -alkyl, C_1 - C_8 -haloalkyl, C_1 - C_8 -alkoxy, C_1 - C_8 -haloalkoxy, C_1 - C_8 -alkylthio, amino, C_1 - C_8 -alkylamino, di(C_1 - C_8 -alkyl)amino or phenyl which may be substituted by halogen, C_1 - C_8 -alkyl, C_1 - C_8 -haloalkyl, C_1 - C_8 -alkoxy, C_1 - C_8 -haloalkoxy or C_1 - C_8 -alkylthio;

m is 0 or 1;

10 R^5 is one of the groups mentioned under R^4 ;

A is a direct bond, -O-, -S-, NR^d , CHR^e or -O- CHR^e ;

15 R^d, R^e are one of the groups mentioned under R^a ;

R^6 is phenyl or a five- or six-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N or S, where the groups R^6 are unsubstituted or may be substituted by one to three R^f ;

20 R^f is one of the groups mentioned under R^b or amino, C_1 - C_8 -alkylamino, di(C_1 - C_8 -alkyl)amino, C_1 - C_8 -haloalkyl, C_1 - C_8 -alkoxyalkyl, C_2 - C_8 -alkenyloxyalkyl, C_2 - C_8 -alkynyloxyalkyl, C_1 - C_8 -alkylcarbonyloxy- C_1 - C_8 -alkyl, cyanoxy- C_1 - C_8 -alkyl, C_3 - C_6 -cycloalkyl or phenoxy, where the cyclic groups may be substituted by halogen, C_1 - C_8 -alkyl, C_1 - C_8 -haloalkyl, C_1 - C_8 -alkoxy, C_1 - C_8 -haloalkoxy or C_1 - C_8 -alkylthio;

30 in a synergistically effective amount.

Moreover, the invention relates to a method for controlling harmful fungi using mixtures of the compound I with the compound II and to the use of the compound I with the compound II for preparing such mixtures and compositions comprising these mixtures.

35 The compound I, 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)[1,2,4]triazolo[1,5-a]pyrimidine, its preparation and its action against harmful fungi are known from the literature (WO 98/46607).

40 The compounds II, their preparation and their action against harmful fungi are likewise known from the literature (WO 00/46184).

Mixtures of triazolopyrimidines with other active compounds are known in a general manner from EP-A 988 790 and US 6 268 371.

- 5 Mixtures of the compounds II with other active compounds are known from WO 03/024219.

10 It was an object of the present invention to provide, with a view to reducing the application rates and broadening the activity spectrum of the known compounds, mixtures which, at a reduced total amount of active compounds applied, have improved activity against harmful fungi (synergistic mixtures).

15 We have found that this object is achieved by the mixtures defined at the outset. Moreover, we have found that simultaneous, that is joint or separate, application of the compound I and one of the compounds II or successive application of the compound I and one of the compounds II allows better control of harmful fungi than is possible with the individual compounds.

20 The mixtures of the compound I and the compound II or the simultaneous, that is joint or separate, use of the compound I and the compound II are distinguished by being highly active against a wide range of phytopathogenic fungi, in particular from the classes of the *Ascomycetes*, *Deuteromycetes*, *Oomycetes* and *Basidiomycetes*. They can be used in crop protection as foliar fungicides, as fungicides for seed dressing and soil-acting fungicides.

25 They are particularly important for controlling a multitude of fungi on various cultivated plants, such as bananas, cotton, vegetable species (for example cucumbers, beans and cucurbits), barley, grass, oats, coffee, potatoes, corn, fruit species, rice, rye, soya, tomatoes, grapevines, wheat, ornamental plants, sugar cane and on a large number of
30 seeds.

They are particularly suitable for the control of the following phytopathogenic fungi:
Blumeria graminis (powdery mildew) on cereals, *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on cucurbits, *Podosphaera leucotricha* on apples, *Uncinula necator* on
35 grapevines, *Puccinia* species on cereals, *Rhizoctonia* species on cotton, rice and lawns, *Ustilago* species on cereals and sugar cane, *Venturia inaequalis* on apples, *Bipolaris* and *Drechslera* species on cereals, rice and lawns, *Septoria nodorum* on wheat, *Botrytis cinerea* on strawberries, vegetables, ornamental plants and grapevines, *Mycosphaerella* species on bananas, peanuts and cereals, *Pseudocercospora herpotrichoides* on wheat and barley, *Phakopsora pachyrhizi* and *P. meibomia* on soy-
40

beans, *Pyricularia oryzae* on rice, *Phytophthora infestans* on potatoes and tomatoes, *Pseudoperonospora* species on cucurbits and hops, *Plasmopara viticola* on grapevines, *Alternaria* species on fruit and vegetables and also *Fusarium* and *Verticillium* species.

5

They can also be used in the protection of materials (e.g. the protection of wood), for example against *Paecilomyces variotii*.

10

The compound I and the compounds II can be applied simultaneously, that is jointly or separately, or in succession, the sequence, in the case of separate application, generally not having any effect on the result of the control measures.

15

In the definitions of the variables given for formula II, collective terms were used which are generally representative of the following substituents:

halogen: fluorine, chlorine, bromine and iodine;

20

alkyl: saturated straight-chain or branched hydrocarbon radicals having 1 to 4, 6, 8 or 10 carbon atoms, for example C₁-C₆-alkyl such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

25

30

haloalkyl: straight-chain or branched alkyl groups having 1 to 2, 4 or 6 carbon atoms (as mentioned above), where some or all of the hydrogen atoms in these groups may be replaced by halogen atoms as mentioned above: in particular C₁-C₂-haloalkyl such as chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl or 1,1,1-trifluoroprop-2-yl;

35

40

alkenyl: unsaturated straight-chain or branched hydrocarbon radicals having 2 to 4, 6, 8 or 10 carbon atoms and one or two double bonds in any position, for example C₂-C₆-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-

1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;

haloalkenyl: unsaturated, straight-chain or branched hydrocarbon radicals having 2 to 10 carbon atoms and one or two double bonds in any position (as mentioned above), where some or all of the hydrogen atoms in these groups may be replaced by halogen atoms as mentioned above, in particular by fluorine, chlorine and bromine;

alkynyl: straight-chain or branched hydrocarbon groups having 2 to 4, 6, 8 or 10 carbon atoms and one or two triple bonds in any position, for example C_2 - C_6 -alkynyl, such as ethynyl, 1-propynyl, 2-propynyl, 1-butyne, 2-butyne, 3-butyne, 1-methyl-2-propynyl, 1-pentyne, 2-pentyne, 3-pentyne, 4-pentyne, 1-methyl-2-butyne, 1-methyl-3-butyne, 2-methyl-3-butyne, 3-methyl-1-butyne, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentyne, 1-methyl-3-pentyne, 1-methyl-4-pentyne, 2-methyl-3-pentyne, 2-methyl-4-pentyne, 3-methyl-1-pentyne, 3-methyl-4-pentyne, 4-methyl-1-pentyne, 4-methyl-2-pentyne, 1,1-dimethyl-2-butyne, 1,1-dimethyl-3-butyne, 1,2-dimethyl-3-butyne, 2,2-dimethyl-3-butyne, 3,3-dimethyl-1-butyne, 1-ethyl-2-butyne, 1-ethyl-3-butyne, 2-ethyl-3-butyne and 1-ethyl-1-methyl-2-propynyl;

cycloalkyl: mono- or bicyclic, saturated hydrocarbon groups having 3 to 6 or 8 carbon ring members, for example C_3 - C_8 -cycloalkyl, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl;

five- to ten-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N and S:

- 5- or 6-membered heterocyclyl which contains one to three nitrogen atoms and/or one oxygen or sulfur atom or one or two oxygen and/or sulfur atoms, for example 2-tetrahydrofuranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl, 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1,3-dioxan-5-yl, 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl, 3-hexahydropyridazinyl, 4-hexahydropyridazinyl, 2-hexahydropyrimidinyl, 4-hexahydropyrimidinyl, 5-hexahydropyrimidinyl and 2-piperazinyl;
- 5-membered heteroaryl which contains one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl and 1,3,4-triazol-2-yl;
- 6-membered heteroaryl which contains one to three or one to four nitrogen atoms: 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl and 2-pyrazinyl;

With a view to the intended use of the compounds II, particular preference is given to the following meanings of the substituents, in each case on their own or in combination:

R¹ is hydrogen;

R² is C₁-C₆-alkyl, such as methyl and ethyl, in particular methyl,

R³ is C₁-C₆-alkyl, such as methyl and ethyl, in particular ethyl;

R⁴ is C₁-C₆-alkyl, in particular methyl;

R⁵ is C₁-C₆-alkyl, in particular methyl;

m is 1, where R⁵ is located in the para-position to R⁴;

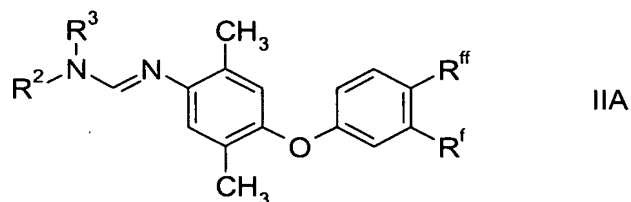
A is oxygen (-O-);

5 R^6 is phenyl which is preferably unsubstituted or substituted by one to three groups R^f , in particular by one or two groups R^f ;

R^f is halogen, in particular fluorine or chlorine, alkyl, in particular methyl, ethyl, n- and isopropyl and tert-butyl, and haloalkyl, in particular trifluoromethyl.

10 The groups R^f are preferably located in the 3- or 3,4-position.

The following compounds of the formula IIA are particularly suitable for the intended use in a mixture with the compound I:



No.	R^2	R^3	R^f	R^{ff}
II-1	CH ₃	CH ₂ CH ₃	CF ₃	Cl
II-2	CH ₃	CH ₂ CH ₃	CF ₃	F
II-3	CH ₃	CH ₃	CF ₃	H
II-4	CH ₂ CH ₃	CH ₂ CH ₃	CF ₃	H
II-5	CH ₃	CH ₃	C(CH ₃) ₃	H
II-6	CH ₂ CH ₃	CH ₂ CH ₃	C(CH ₃) ₃	H
II-7	CH ₃	CH ₃	C ₆ H ₅ -O-	H
II-8	CH ₂ CH ₃	CH ₂ CH ₃	C ₆ H ₅ -O-	H
II-9	CH ₃	CH ₃	Cl	Cl
II-10	CH ₂ CH ₃	CH ₂ CH ₃	Cl	Cl

15

Owing to the basic character of their nitrogen atoms, the compounds I and II are capable of forming salts or adducts with inorganic or organic acids or with metal ions.

20 Examples of inorganic acids are hydrohalic acids, such as hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide, sulfuric acid, phosphoric acid and nitric acid.

25 Suitable organic acids are, for example, formic acid, carbonic acid, and alkanoic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic

acid, p-toluenesulfonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid and 2-acetoxybenzoic acid.

- Suitable metal ions are in particular the ions of the elements of transition groups one to eight, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc, and in addition those of the second main group, in particular calcium and magnesium, and of the third and fourth main group, in particular aluminum, tin and lead. If appropriate, the metal ions can be present in the various valencies that they can assume.
- 10 When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or against other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added according to need.
- 15 When preparing the mixtures, it is preferred to employ the pure active compounds I and II, to which further active compounds against harmful fungi or against other pests, such as insects, arachnids or nematodes, or else herbicidal or growth-regulating active compounds or fertilizers can be added according to need.
- 20 Other suitable active compounds in the above sense are in particular fungicides selected from the following group:
- acylalanines, such as benalaxyl, metalaxyl, ofurace, oxadixyl,
 - amine derivatives, such as aldimorph, dodine, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, spiroxamine, tridemorph,
 - anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinil,
 - antibiotics, such as cycloheximid, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
 - azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, ipconazole, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizol, triticonazole,
 - dicarboximides, such as iprodione, myclozolin, procymidone, vinclozolin,
 - dithiocarbamates, such as ferbam, nabam, maneb, mancozeb, metam, metiram, propineb, polycarbamate, thiram, ziram, zineb,
 - heterocyclic compounds, such as anilazine, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadone, fenamidone, fenarimol, fuberidazole, flutolanil, furametpyr, isoprothiolan, mepronil, nuarimol, penthiopyrad, picobenzamid, probenazole, proquinazid, pyrifenoxy, pyroquilon, qui-

- noxyfen, silthiofam, thiabendazole, thifluzamid, thiophanate-methyl, tiadinil, tricyclazole, triforine,
- copper fungicides, such as Bordeaux mixture, copper acetate, copper oxychloride, basic copper sulfate,
 - 5 • nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton, nitrophthalisopropyl,
 - phenylpyrroles, such as fenpiclonil or fludioxonil,
 - sulfur,
 - other fungicides, such as acibenzolar-S-methyl, benthiavalicarb, carpropamid,
 - 10 chlorothalonil, cyflufenamid, cymoxanil, diclomezin, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin acetate, fenoxanil, ferimzone, fluazinam, fosetyl, fosetyl-aluminum, phosphorous acid, iprovalicarb, hexachlorobenzene, metrafenon, pencycuron, propamocarb, phthalide, toloclofos-methyl, quintozone, zoxamid,
 - 15 • strobilurins, such as azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin or trifloxystrobin,
 - sulfenic acid derivatives, such as captafol, captan, dichlofluanid, folpet, tolylfluanid,
 - cinnamides and analogous compounds, such as dimethomorph, flumetover or flumorph.
 - 20

In one embodiment of the mixtures according to the invention, a further fungicide III or two fungicides III and IV are added to the compounds I and II.

- 25 Preference is given to mixtures of the compounds I and II and a component III. Particular preference is given to mixtures of the compounds I and II.

The compound I and the compound II are usually applied in a weight ratio of from 100:1 to 1:100, preferably from 20:1 to 1:20, in particular from 10:1 to 1:10.

30

The components III and, if appropriate, IV are, if desired, added in a ratio of 20:1 to 1:20 to the compound I.

- 35 Depending on the type of compound and the desired effect, the application rates of the mixtures according to the invention are from 5 g/ha to 1000 g/ha, preferably from 50 to 900 g/ha, in particular from 50 to 750 g/ha.

Correspondingly, the application rates for the compound I are generally from 1 to 1000 g/ha, preferably from 10 to 900 g/ha, in particular from 20 to 750 g/ha.

40

Correspondingly, the application rates for the compound II are generally from 1 to 1000 g/ha, preferably from 10 to 500 g/ha, in particular from 40 to 350 g/ha.

5 In the treatment of seed, application rates of mixture are generally from 1 to 1000 g/100 kg of seed, preferably from 1 to 200 g/100 kg, in particular from 5 to 100 g/100 kg.

10 The method for controlling harmful fungi is carried out by the separate or joint application of the compound I and the compound II or of the mixtures of the compound I and the compound II, by spraying or dusting the seeds, the plants or the soils before or after sowing of the plants or before or after emergence of the plants.

15 The mixtures according to the invention, or the compounds I and II, can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The use form depends on the particular intended purpose; in each case, it should ensure a fine and even distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants.

20 Solvents/auxiliaries suitable for this purpose are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used,
 - carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionogenic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignosulfite waste liquors and methylcellulose.
- 30

Suitable surfactants used are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether,

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tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lagnosulfite waste liquors and methylcellulose.

5

Substances which are suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, highly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

10

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Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

20

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

25

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compounds. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

30

The following are examples of formulations: 1. Products for dilution with water

A) Water-soluble concentrates (SL)

10 parts by weight of the active compounds are dissolved in water or in a water-soluble solvent. As an alternative, wetting agents or other auxiliaries are added. The active compound dissolves upon dilution with water.

35

B) Dispersible concentrates (DC)

20 parts by weight of the active compounds are dissolved in cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

40

C) Emulsifiable concentrates (EC)

15 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength).

5 Dilution with water gives an emulsion.

D) Emulsions (EW, EO)

40 parts by weight of the active compounds are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5% strength).

10 This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E) Suspensions (SC, OD)

15 In an agitated ball mill, 20 parts by weight of the active compounds are comminuted with addition of dispersants, wetting agents and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F) Water-dispersible granules and water-soluble granules (WG, SG)

20 50 parts by weight of the active compounds are ground finely with addition of dispersants and wetting agents and prepared as water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

25

G) Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of the active compounds are ground in a rotor-stator mill with addition of dispersants, wetting agents and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

30

2. Products to be applied undiluted

H) Dustable powders (DP)

35 5 parts by weight of the active compounds are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I) Granules (GR, FG, GG, MG)

40 0.5 part by weight of the active compounds is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J) ULV solutions (UL)

10 parts by weight of the active compounds are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

5

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended purposes; they are intended to ensure in each case the finest possible distribution of the active compounds according to the invention.

10

15

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetting agent, tackifier, dispersant or emulsifier. However, it is also possible to prepare concentrates composed of active substance, wetting agent, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

20

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

25

The active compounds may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

30

Oils of various types, wetting agents, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, even, if appropriate, not until immediately prior to use (tank mix). These agents are typically admixed with the compositions according to the invention in a weight ratio of from 1:10 to 10:1.

35

The compounds I and II or the mixtures or the corresponding formulations are applied by treating the harmful fungi, the plants, seeds, soils, areas, materials or spaces to be kept free from them with a fungicidally effective amount of the mixture or, in the case of separate application, of the compounds I and II. Application can be carried out before or after infection by the harmful fungi.

40

The fungicidal effect of the compound and the mixtures is demonstrated by the following tests:

The active compounds, separately, were prepared as a stock solution comprising
5 25 mg of active compound which was made up to 10 ml using a mixture of acetone
and/or DMSO and the emulsifier Uniperol® EL (wetting agent having an emulsifying
and dispersing action based on ethoxylated alkylphenols) in a ratio by volume of
solvent/emulsifier of 99:1. The mixture was then made up to 100 ml with water. The
active compounds or mixtures were diluted or mixed with water to the stated
10 concentration.

Activity against net blotch of barley caused by *Pyrenophora teres*, 1 day protective
application

15 Leaves of potted barley seedlings of the "Hanna" cultivar were sprayed to runoff point
with an aqueous suspension having the concentration of active compound stated
below. 24 hours after the spray coating had dried on, the test plants were inoculated
with an aqueous spore suspension of *Pyrenophora* [syn. *Drechslera*] *teres*, the net
blotch pathogen. The test plants were then placed in a greenhouse at temperatures
20 between 20 and 24°C and 95 to 100% relative atmospheric humidity. After 6 days, the
extent of the development of the disease was determined visually in % infection of the
total leaf area.

The visually determined percentages of infected leaf areas were converted into
25 efficacies in % of the untreated control:

The efficacy (E) is calculated as follows using Abbot's formula:

$$E = (1 - \alpha/\beta) \cdot 100$$

30

α corresponds to the fungal infection of the treated plants in % and
 β corresponds to the fungal infection of the untreated (control) plants in %

An efficacy of 0 means that the infection level of the treated plants corresponds to that
35 of the untreated control plants; an efficacy of 100 means that the treated plants were
not infected.

The expected efficacies of mixtures of active compounds were determined using
Colby's formula (Colby, S.R. "Calculating synergistic and antagonistic responses of
40 herbicide combinations", Weeds, 15, 20-22, 1967) and compared with the observed

efficacies.

Colby's formula:

$$E = x + y - x \cdot y / 100$$

E expected efficacy, expressed in % of the untreated control, when using the

mixture of the active compounds A and B at the concentrations a and b

x efficacy, expressed in % of the untreated control, when using the active

10 compound A at the concentration a

y efficacy, expressed in % of the untreated control, when using the active
compound B at the concentration b

Table A – Individual active compounds

Example	Active compound/ mixing ratio	Concentration of active compound in the spray liquor [ppm]	Efficacy in % of the un- treated control
1	control (untreated)	-	(89 % infection)
2	I	5 1.25	78 55
3	II-6	5 1.25	0 0

Table B – Mixtures according to the invention

Example	Active compound mixture Concentration Mixing ratio	Observed efficacy	Calculated efficacy*)
4	I + II-6 5 + 1.25 ppm 4:1	100	78
5	I + II-6 1.25 + 5 ppm 1:4	83	55

*) Efficacy calculated using Colby's formula

20 The test results show that, by virtue of strong synergism, the mixtures according to the
invention have, in all mixing ratios, considerably better activity than had been predicted
using Colby's formula.